PRODUCTION OF SILICON CARBIDE SINGLE CRYSTAL

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Applicant: NIPPON STEEL CORP

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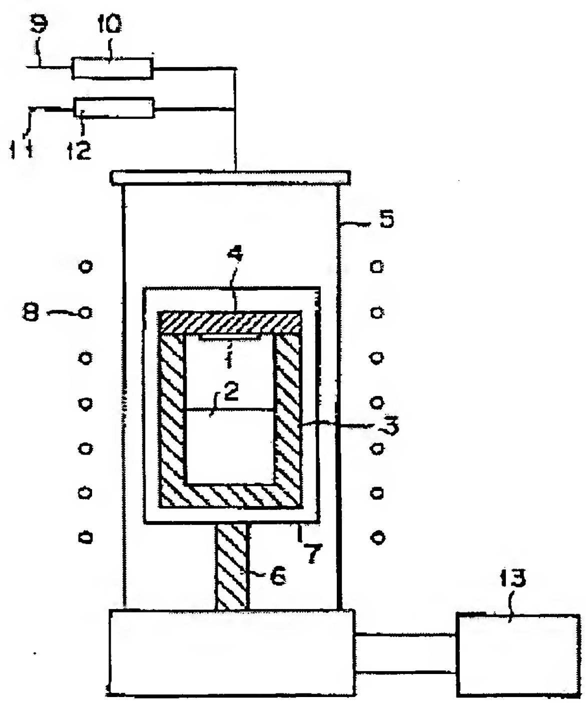
Abstract of **JP9157092**

PROBLEM TO BE SOLVED: To decrease micropipe-like defects when a silicon carbide single crystal is grown by sublimation recrystallization method with using a seed crystal, by incorporating impurity elements in the growing atmosphere to supply a large amt. of impurities in the growing crystal.
SOLUTION: A substrate 1 comprising silicon carbide is prepared as a seed crystal and attached to the inner face of a lid 4 of a crucible 3. After a source material 2 comprising a silicon carbide powder is supplied in the crucible 3, the crucible 3 is disposed in a double quartz tube 5. After the quartz tube 5 is evacuated, a work coil 8 is energized to heat the source material 2 to about 2000 deg.C. Then an atmosphere gas containing impurity atoms such as nitrogen in an amt. preferably >=10<19> cm<-3> is introduced into the tube 5 to grow a silicon carbide single crystal by sublimation recrystallization method, while a large amt. of impurities is introduced into the growing surface and the growing crystal. Thereby, micropipe-like defects can be decreased and the obtd. silicon carbide single crystal can be used as a light-emitting element for blue colors having excellent optical characteristics.



JAPANESE [JP,09-157092,A]

CLAIMS DETAILED DESCRIPTION TECHNICAL FIELD PRIOR ART EFFECT OF THE INVENTION TECHNICAL PROBLEM MEANS DESCRIPTION OF DRAWINGS DRAWINGS

[Translation done.]

CLAIMS

[Claim(s)]
[Claim 1] How to make an impurity element contain in a growth ambient atmosphere, to supply a growth front face and a lot of impurities during a growth crystal in the approach of growing up silicon carbide monocrystal by the sublimation recrystallizing method using seed crystal, and to grow up silicon carbide monocrystal with few micro pipe defects.
[Claim 2] The manufacture approach of the single crystal silicon carbide according to claim 1 characterized by growing up silicon carbide monocrystal with few micro pipe defects by making high concentration contain nitrogen, aluminum, or a boron atom as an impurity in said growth ambient atmosphere, consequently making nitrogen, aluminum, or a boron atom contain three or more [1019cm -] in silicon carbide monocrystal.

[Translation done.]

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DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention] Especially this invention relates to the growth approach of the good and large-sized single crystal ingot used as substrate wafers, such as a blue light emitting diode and an electron device, with respect to the manufacture approach of silicon carbide monocrystal.
[0002]
[Description of the Prior Art] Silicon carbide (SiC) is excellent also in thermal resistance and a mechanical strength, and attracts attention as an environment-resistant semiconductor material from physical and chemical property, like it is strong in a radiation. At the room temperature, especially the silicon carbide crystal of 6H mold has forbidden-band width of face of about 3eV, and is used as a blue light emitting diode ingredient.
[0003] However, the crystal growth technique which can supply the silicon carbide monocrystal of the high quality which has a large area to stability on a scale of industrial is not yet established. So, the utilization was obstructed in spite of the semiconductor material with which silicon carbide has the advantage and possibility of above many.
[0004] Conventionally, on a scale of laboratory extent, silicon carbide monocrystal was grown up, for example by the sublimation recrystallizing method (Rayleigh law), and the silicon carbide monocrystal of the size which can produce a semiconductor device had been obtained. However, the area of the single crystal obtained by this approach is small, and it is difficult to control that dimension and configuration to high degree of accuracy. Moreover, control of the crystal polymorphism which silicon carbide has, and impurity carrier concentration is not easy, either.
[0005] Moreover, growing up cubic silicon carbide monocrystal is also performed by carrying out heteroepitaxial growth on different-species substrates, such as silicon (Si) **, using a chemical-vapor-deposition method (CVD method). Although the single crystal of a large area is obtained by this approach, it is not easy for grid mismatching with a substrate to be unable to grow up only the silicon carbide monocrystal which includes many defects by a certain thing etc. (- 107cm- 2), and to obtain the silicon carbide monocrystal of high quality about 20%.
[0006] advanced Rayleigh who uses seed crystal and performs sublimation recrystallization in order to solve these troubles -- law is proposed (Yu.M.Tairov and V.F.Tsvetkov, Journal of Crystal Growth vol.52 (1981) pp.146-150). By this approach, since seed crystal is used, control of the nucleation process of a crystal is possible, and a crystal growth rate etc. can be controlled with sufficient repeatability by controlling an ambient atmosphere pressure from Number Torr to 100Torr extent with inert gas. Furthermore, the resistivity of impurities of a crystal, i.e., the amount under crystal, is controllable by adding impurity gas in the ambient atmosphere which consists of inert gas, or mixing an impurity element or its compound in silicon carbide raw material powder. Under the present circumstances, Koga Sum happiness, the 39th volume of semi-conductor research The resistivity of a crystal was controlled in the range of 0.04-200-ohmcm by introducing nitrogen, aluminum, or a boron atom into a crystal 1016-1019cm-3 as indicated by p.151.
[0007] Thus, if the sublimation recrystallizing method using seed crystal is used, large-sized silicon carbide monocrystal can be grown up with sufficient repeatability, controlling a crystal polymorphism (polytype), a configuration, and resistivity.
[0008]
[Problem(s) to be Solved by the Invention] When silicon carbide monocrystal was grown up by the above-mentioned conventional approach, the pinhole with a diameter of several microns which penetrates the crystal called a micro pipe defect in the growth direction was included in the growth crystal about [102-103cm -] two. P.G. When these defects

produce a component, the leakage current etc. is caused and let the reduction be a problem of the utmost importance in device application of silicon carbide monocrystal, as indicated by Neudeck et al. and IEEE Electron Device Letters vol.15 (1994) pp.63-65.
[0009] This micro pipe defect is generated with the swirl growth which is in typical growth mode in silicon carbide monocrystal as shown in J.Takahashi et al. and Journal of Crystal Growth vol.135 (1994) pp.61-70.
[0010] This invention is made in view of the above-mentioned situation, and offers the manufacture approach of silicon carbide monocrystal that the single crystal ingot with them which can cut down a large-sized wafer can be manufactured with sufficient repeatability. [there are few defects and good]
[0011]
[Means for Solving the Problem] This invention for attaining the above-mentioned object is constituted as follows.
[0012] Invention according to claim 1 is the approach of making an impurity element containing in a growth ambient atmosphere, supplying a growth front face and a lot of impurities during a growth crystal, and growing up silicon carbide monocrystal with few micro pipe defects, in the approach of growing up silicon carbide monocrystal by the sublimation recrystallizing method for having used seed crystal.
[0013] Invention according to claim 2 is the manufacture approach of the single crystal silicon carbide according to claim 1 characterized by growing up silicon carbide monocrystal with few micro pipe defects by making high concentration contain nitrogen, aluminum, or a boron atom as an impurity in said growth ambient atmosphere, consequently making nitrogen, aluminum, or a boron atom contain three or more [1019cm -] in silicon carbide monocrystal.
[0014] By the manufacture approach of the single crystal silicon carbide of this invention carrying out heating sublimation of the raw material which consists of silicon carbide, supplying it on the seed crystal which consists of silicon carbide monocrystal, and making high concentration contain an impurity in a growth ambient atmosphere in the approach of growing up silicon carbide monocrystal on this seed crystal, a lot of impurities are supplied to a growth front face, and the high impurity concentration under crystal grows three or more [1019cm -] silicon carbide monocrystal.
[0015]
[Embodiment of the Invention] By the manufacture approach of this invention, by making an impurity contain by high concentration and supplying a lot of impurities on a growth front face into a growth ambient atmosphere, the swirl growth which is in typical growth mode of silicon carbide monocrystal tends to be controlled, and it is going to prevent generating of a micro pipe. After the molecular species which contributes to growth diffuses a front-face top enough, swirl growth reaches the step formed in the front face of screw dislocation, and takes place by being incorporated at a crystal lattice. This is equivalent to the crystal growth format usually called step flow mode. Since the surface diffusion of the molecular species which contributes to growth was checked and an impurity served as a kind of effective two-dimensional-nucleus formation further when a lot of impurities exist in a front face, this step flow mode could not happen easily and artificers found out that micro pipe generating was controlled. When the molecular species which contributes to growth does not reach a step but this causes two-dimensional-nucleus formation on a front face, the step formed in the front face of screw dislocation is because it is succeeded in a configuration as it is and swirl growth is controlled as a result, without whirling around.
[0016] Moreover, during the silicon carbide growth by the amelioration Rayleigh method, as a result of supplying an impurity to a front face so much, silicon carbide will contain a high-concentration impurity (3 or more [1019cm -]), and the surface energy increases. According to Frank (F. C.Frank, Acta Cryst.vol.4 (1951) pp.497-501), by the large matter of surface energy, the diameter of a micro pipe becomes small. Therefore, according to this invention, it is possible it not only can to control generating of a micro pipe, but to make the path of the generated micro pipe small and to reduce the effect on a device.
[0017] As an approach of making high concentration containing an impurity in a growth ambient atmosphere, two, the approach of introducing into a reaction vessel with inert gas as gas and the approach of making it contain beforehand in a silicon carbide powder raw material, can be considered. Moreover, although installation of the impurity to such silicon carbide monocrystal is the object to which the electrical characteristics (a conduction type, resistivity) of a crystal are changed and it was usually conventionally carried out in the 1016cm-three to three or less [1019cm -] range, it is not used in the three or more [1019cm -] range for the purpose of control of a crystal defect like this invention.

[0018]
[Example 1] advanced Rayleigh for whom drawing 1 used seed crystal -- it is an example of the manufacturing installation used for this invention into which single crystal silicon carbide is grown up by law.
[0019] First, this single crystal growth equipment is explained briefly. Crystal growth is performed on the silicon-carbide-monocrystal substrate 1 used as seed crystal by carrying out sublimation recrystallization of the silicon carbide powder 2 which is a raw material. The silicon carbide crystal substrate 1 of seed crystal is attached in the inner surface of the lid 4 of the crucible 3 made from a graphite. The interior of the crucible 3 made from a graphite is filled up with the silicon carbide powder 2 of a raw material. Such crucible 3 made from a graphite is installed in the interior of the duplex quartz tube 5 by the bearing bar 6 of a graphite. The felt 7 made from a graphite for a heat-shield is installed in the perimeter of the crucible 3 made from a graphite. The duplex quartz tube 5 can carry out high vacuum exhaust air (10 to 5 or less Torrs) with evacuation equipment, and can carry out pressure control of the internal ambient atmosphere to Ar with the mixed gas of dopant gas. Moreover, the work-piece coil 8 is installed in the periphery of the duplex quartz tube 5, by passing the high frequency current, the crucible 3 made from a graphite can be heated and a raw material and seed crystal can be heated to desired temperature. Measurement of crucible temperature prepares an optical path with a diameter of 2-4mm for the crucible upper part and the lower part in the center section of the wrap felt, takes out the light from the crucible upper part and the lower part, and is performed using a two-color thermometer. Raw material temperature and temperature of the crucible upper part are made into seed temperature for the temperature of the crucible lower part.
[0020] Next, an example is explained about manufacture of the silicon carbide monocrystal using this crystal growth equipment.
[0021] First, the substrate 1 with which growth side bearing consists of silicon carbide of the hexagonal system which is the <0001> directions as seed crystal was prepared. And this substrate 1 was attached in the inner surface of the lid 4 of the crucible 3 made from a graphite. Moreover, the interior of the crucible 3 made from a graphite was filled up with the raw material 2. Subsequently, after the lid 4 furnished with seed crystal covered the crucible 3 made from a graphite filled up with the raw material with closing and the felt 7 made from a graphite, it was put on the bearing bar 6 made from a graphite, and was installed in the interior of the duplex quartz tube 5. And after carrying out evacuation of the interior of a quartz tube, sink raw material temperature was raised for the current to the work-piece coil to 2000-degree Centigrade. Then, raw material temperature was raised to the 2400-degree Centigrade which is target temperature, making the mixed gas which contained nitrogen gas in Ar gas 75% as a controlled atmosphere flow, and maintaining quartz tube internal pressure at about 600 Torr(s). To 20Torr(s) which are growth pressures, it decompressed over about 30 minutes, and growth was continued after that for about 20 hours. The growth rate in this case was about 1mm per hour. It is necessary to inert gas, such as Ar gas, to set the rate of the nitrogen gas under growth as 10 - 100% of range. By low concentration, supply of a dopant on a front face is inadequate, the diffusion prevention effectiveness of the molecular species which contributes to growth cannot be expected, and the nitrogen concentration in a single crystal does not become three or more [1019cm -] from this, either. Moreover, if the partial pressure in the reaction vessel of nitrogen is set to 40 or more Torrs, the nitrogen on a growth front face will come to have an adverse effect on crystallinity. That is, polycrystal-ization etc. comes to take place.
[0022] In this way, when an X diffraction and Raman scattering analyzed the obtained silicon carbide monocrystal, it has checked that the silicon carbide monocrystal of hexagonal system had grown. The grown-up crystal was more uniform than the seed crystal top to the growth outermost surface, and there were also dramatically few abnormalities about carbon, and it was silicon carbide monocrystal of high quality. Furthermore, when the nitrogen concentration under crystal was investigated according to secondary ion mass spectrometry, it was 2x1020cm-3.
[0023] Moreover, it considered as the {0001} side wafer by cutting and grinding the grown-up single crystal ingot in order to evaluate a micro pipe defect. Then, when the wafer front face was etched by the melting KOH of about 530 Centigrade and the microscope investigated the number of the forward large-sized hexagon etch pits corresponding to a micro pipe defect, it turned out that the micro pipe defect has reduced only Ar by half compared with the case where it uses as a controlled atmosphere. Moreover, that the path of the generated micro pipe is decreasing has checked by microscope observation of the front face before etching.
[0024]
[Example 2] The substrate 1 with which growth side bearing consists of silicon carbide of the hexagonal system which is the <0001> directions as seed crystal as well as an example 1 was prepared, and seed crystal was attached in the

inner surface of the lid 4 of the crucible 3 made from a graphite. Next, although the interior of the crucible 3 made from a graphite was filled up with the raw material 2, the carbide (B4C) of the boron which is the impurity of P type was mixed 0.25% of the weight in the silicon carbide raw material in this case. (4) which generally mixes the compound containing (3) dopant element which uses for a raw material what sintered further the mixture of (2) and (1) which mix the (1) dopant element itself in a silicon carbide raw material as the method of mixing to the silicon carbide raw material of a dopant atom (equivalent to this example) -- the four approaches of ** using the silicon carbide raw material which doped the dopant element beforehand can be considered.

[0025] Evacuation after raw material restoration, temperature control, pressure control, etc. were performed almost like the example 1. However, the controlled atmosphere was made into Ar100%. It is necessary to set it as 0.1 - 1% of range as a charge of B4C in a silicon carbide raw material. The low concentration of supply of a dopant on a front face is more inadequate than this, the diffusion prevention effectiveness of the molecular species which contributes to growth cannot be expected, and good single crystal growth cannot be realized by high concentration from this.

[0026] In this way, when an X diffraction and Raman scattering analyzed the obtained silicon carbide monocrystal, it has checked that the silicon carbide monocrystal of hexagonal system had grown. The grown-up crystal was more uniform than the seed crystal top to the growth outermost surface, and there were also dramatically few abnormalities about carbon, and it was silicon carbide monocrystal of high quality.

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PRIOR ART

[Description of the Prior Art] Silicon carbide (SiC) is excellent also in thermal resistance and a mechanical strength, and attracts attention as an environment-resistant semiconductor material from physical and chemical property, like it is strong in a radiation. At the room temperature, especially the silicon carbide crystal of 6H mold has forbidden-band width of face of about 3eV, and is used as a blue light emitting diode ingredient.
[0003] However, the crystal growth technique which can supply the silicon carbide monocrystal of the high quality which has a large area to stability on a scale of industrial is not yet established. So, the utilization was obstructed in spite of the semiconductor material with which silicon carbide has the advantage and possibility of above many.
[0004] Conventionally, on a scale of laboratory extent, silicon carbide monocrystal was grown up, for example by the sublimation recrystallizing method (Rayleigh law), and the silicon carbide monocrystal of the size which can produce a semiconductor device had been obtained. However, the area of the single crystal obtained by this approach is small, and it is difficult to control that dimension and configuration to high degree of accuracy. Moreover, control of the crystal polymorphism which silicon carbide has, and impurity carrier concentration is not easy, either.
[0005] Moreover, growing up cubic silicon carbide monocrystal is also performed by carrying out heteroepitaxial growth on different-species substrates, such as silicon (Si) **, using a chemical-vapor-deposition method (CVD method). Although the single crystal of a large area is obtained by this approach, it is not easy for grid mismatching with a substrate to be unable to grow up, only the silicon carbide monocrystal which includes many defects by a certain thing etc. (- 107cm- 2), and to obtain the silicon carbide monocrystal of high quality about 20%.
[0006] advanced Rayleigh who uses seed crystal and performs sublimation recrystallization in order to solve these troubles -- law is proposed (Yu.M.Tairov and V.F.Tsvetkov, Journal of Crystal Growth vol.52 (1981) pp.146-150). By this approach, since seed crystal is used, control of the nucleation process of a crystal is possible, and a crystal growth rate etc. can be controlled with sufficient repeatability by controlling an ambient atmosphere pressure from Number Torr to 100Torr extent with inert gas. Furthermore, the resistivity of impurities of a crystal, i.e., the amount under crystal, is controllable by adding impurity gas in the ambient atmosphere which consists of inert gas, or mixing an impurity element or its compound in silicon carbide raw material powder. Under the present circumstances, Koga Sum happiness, the 39th volume of semi-conductor research The resistivity of a crystal was controlled in the range of 0.04-200-ohmcm by introducing nitrogen, aluminum, or a boron atom into a crystal 1016-1019cm-3 as indicated by p.151.
[0007] Thus, if the sublimation recrystallizing method using seed crystal is used, large-sized silicon carbide monocrystal can be grown up with sufficient repeatability, controlling a crystal polymorphism (polytype), a configuration, and resistivity.

[Translation done.]

EFFECT OF THE INVENTION

[Effect of the Invention] advanced Rayleigh using seed crystal according to [as explained above] claim 1 and invention according to claim 2 -- in law, swirl growth can be controlled and good silicon carbide monocrystal with few micro pipes which these become a cause and are generated can be grown up with repeatability and sufficient homogeneity.
[0029] If a silicon-carbide-monocrystal thin film is grown up on this substrate by the vapor-phase-epitaxial-growth method, using such silicon carbide monocrystal as a substrate for growth, the high proof pressure and environment-resistant electron device which was excellent in the blue light emitting device which was excellent in the optical property, and electrical characteristics can be manufactured.

[Translation done.]

TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention] When silicon carbide monocrystal was grown up by the above-mentioned conventional approach, the pinhole with a diameter of several microns which penetrates the crystal called a micro pipe defect in the growth direction was included in the growth crystal about [102-103cm -] two. P.G. When these defects produce a component, the leakage current etc. is caused and let the reduction be a problem of the utmost importance in device application of silicon carbide monocrystal, as indicated by Neudeck et al. and IEEE Electron Device Letters vol.15 (1994) pp.63-65.
[0009] This micro pipe defect is generated with the swirl growth which is in typical growth mode in silicon carbide monocrystal as shown in J.Takahashi et al. and Journal of Crystal Growth vol.135 (1994) pp.61-70.
[0010] This invention is made in view of the above-mentioned situation, and offers the manufacture approach of silicon carbide monocrystal that the single crystal ingot with them which can cut down a large-sized wafer can be manufactured with sufficient repeatability. [there are few defects and good]

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MEANS

[Means for Solving the Problem] This invention for attaining the above-mentioned object is constituted as follows.
[0012] Invention according to claim 1 is the approach of making an impurity element containing in a growth ambient atmosphere, supplying a growth front face and a lot of impurities during a growth crystal, and growing up silicon carbide monocrystal with few micro pipe defects, in the approach of growing up silicon carbide monocrystal by the sublimation recrystallizing method for having used seed crystal.
[0013] Invention according to claim 2 is the manufacture approach of the single crystal silicon carbide according to claim 1 characterized by growing up silicon carbide monocrystal with few micro pipe defects by making high concentration contain nitrogen, aluminum, or a boron atom as an impurity in said growth ambient atmosphere, consequently making nitrogen, aluminum, or a boron atom contain three or more [1019cm -] in silicon carbide monocrystal.
[0014] By the manufacture approach of the single crystal silicon carbide of this invention carrying out heating sublimation of the raw material which consists of silicon carbide, supplying it on the seed crystal which consists of silicon carbide monocrystal, and making high concentration contain an impurity in a growth ambient atmosphere in the approach of growing up silicon carbide monocrystal on this seed crystal, a lot of impurities are supplied to a growth front face, and the high impurity concentration under crystal grows three or more [1019cm -] silicon carbide monocrystal.
[0015]
[Embodiment of the Invention] By the manufacture approach of this invention, by making an impurity contain by high concentration and supplying a lot of impurities on a growth front face into a growth ambient atmosphere, the swirl growth which is in typical growth mode of silicon carbide monocrystal tends to be controlled, and it is going to prevent generating of a micro pipe. After the molecular species which contributes to growth diffuses a front-face top enough, swirl growth reaches the step formed in the front face of screw dislocation, and takes place by being incorporated at a crystal lattice. This is equivalent to the crystal growth format usually called step flow mode. Since the surface diffusion of the molecular species which contributes to growth was checked and an impurity served as a kind of effective two-dimensional-nucleus formation further when a lot of impurities exist in a front face, this step flow mode could not happen easily and artificers found out that micro pipe generating was controlled. When the molecular species which contributes to growth does not reach a step but this causes two-dimensional-nucleus formation on a front face, the step formed in the front face of screw dislocation is because it is succeeded in a configuration as it is and swirl growth is controlled as a result, without whirling around.
[0016] Moreover, during the silicon carbide growth by the amelioration Rayleigh method, as a result of supplying an impurity to a front face so much, silicon carbide will contain a high-concentration impurity (3 or more [1019cm -]), and the surface energy increases. According to Frank (F. C.Frank, Acta Cryst.vol.4 (1951) pp.497-501), by the large matter of surface energy, the diameter of a micro pipe becomes small. Therefore, according to this invention, it is possible it not only can to control generating of a micro pipe, but to make the path of the generated micro pipe small and to reduce the effect on a device.
[0017] As an approach of making high concentration containing an impurity in a growth ambient atmosphere, two, the approach of introducing into a reaction vessel with inert gas as gas and the approach of making it contain beforehand in a silicon carbide powder raw material, can be considered. Moreover, although installation of the impurity to such silicon carbide monocrystal is the object to which the electrical characteristics (a conduction type, resistivity) of a

crystal are changed and it was usually conventionally carried out in the 1016cm-three to three or less [1019cm -] range, it is not used in the three or more [1019cm -] range for the purpose of control of a crystal defect like this invention.

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[Example 1] advanced Rayleigh for whom drawing 1 used seed crystal -- it is an example of the manufacturing installation used for this invention into which single crystal silicon carbide is grown up by law.

[0019] First, this single crystal growth equipment is explained briefly. Crystal growth is performed on the silicon-carbide-monocrystal substrate 1 used as seed crystal by carrying out sublimation recrystallization of the silicon carbide powder 2 which is a raw material. The silicon carbide crystal substrate 1 of seed crystal is attached in the inner surface of the lid 4 of the crucible 3 made from a graphite. The interior of the crucible 3 made from a graphite is filled up with the silicon carbide powder 2 of a raw material. Such crucible 3 made from a graphite is installed in the interior of the duplex quartz tube 5 by the bearing bar 6 of a graphite. The felt 7 made from a graphite for a heat-shield is installed in the perimeter of the crucible 3 made from a graphite. The duplex quartz tube 5 can carry out high vacuum exhaust air (10 to 5 or less Torrs) with evacuation equipment, and can carry out pressure control of the internal ambient atmosphere to Ar with the mixed gas of dopant gas. Moreover, the work-piece coil 8 is installed in the periphery of the duplex quartz tube 5, by passing the high frequency current, the crucible 3 made from a graphite can be heated and a raw material and seed crystal can be heated to desired temperature. Measurement of crucible temperature prepares an optical path with a diameter of 2-4mm for the crucible upper part and the lower part in the center section of the wrap felt, takes out the light from the crucible upper part and the lower part, and is performed using a two-color thermometer. Raw material temperature and temperature of the crucible upper part are made into seed temperature for the temperature of the crucible lower part.

[0020] Next, an example is explained about manufacture of the silicon carbide monocrystal using this crystal growth equipment.

[0021] First, the substrate 1 with which growth side bearing consists of silicon carbide of the hexagonal system which is the <0001> directions as seed crystal was prepared. And this substrate 1 was attached in the inner surface of the lid 4 of the crucible 3 made from a graphite. Moreover, the interior of the crucible 3 made from a graphite was filled up with the raw material 2. Subsequently, after the lid 4 furnished with seed crystal covered the crucible 3 made from a graphite filled up with the raw material with closing and the felt 7 made from a graphite, it was put on the bearing bar 6 made from a graphite, and was installed in the interior of the duplex quartz tube 5. And after carrying out evacuation of the interior of a quartz tube, sink raw material temperature was raised for the current to the work-piece coil to 2000-degree Centigrade. Then, raw material temperature was raised to the 2400-degree Centigrade which is target temperature, making the mixed gas which contained nitrogen gas in Ar gas 75% as a controlled atmosphere flow, and maintaining quartz tube internal pressure at about 600 Torr(s). To 20Torr(s) which are growth pressures, it decompressed over about 30 minutes, and growth was continued after that for about 20 hours. The growth rate in this case was about 1mm per hour. It is necessary to inert gas, such as Ar gas, to set the rate of the nitrogen gas under growth as 10 - 100% of range. By low concentration, supply of a dopant on a front face is inadequate, the diffusion prevention effectiveness of the molecular species which contributes to growth cannot be expected, and the nitrogen concentration in a single crystal does not become three or more [1019cm -] from this, either. Moreover, if the partial pressure in the reaction vessel of nitrogen is set to 40 or more Torrs, the nitrogen on a growth front face will come to have an adverse effect on crystallinity. That is, polycrystal-ization etc. comes to take place.

[0022] In this way, when an X diffraction and Raman scattering analyzed the obtained silicon carbide monocrystal, it has checked that the silicon carbide monocrystal of hexagonal system had grown. The grown-up crystal was more uniform than the seed crystal top to the growth outermost surface, and there were also dramatically few abnormalities about carbon, and it was silicon carbide monocrystal of high quality. Furthermore, when the nitrogen concentration under crystal was investigated according to secondary ion mass spectrometry, it was 2x1020cm-3.

[0023] Moreover, it considered as the {0001} side wafer by cutting and grinding the grown-up single crystal ingot in order to evaluate a micro pipe defect. Then, when the wafer front face was etched by the melting KOH of about 530 Centigrade and the microscope investigated the number of the forward large-sized hexagon etch pits corresponding to a micro pipe defect, it turned out that the micro pipe defect has reduced only Ar by half compared with the case where it uses as a controlled atmosphere. Moreover, that the path of the generated micro pipe is decreasing has checked by microscope observation of the front face before etching.

[0024]
[Example 2] The substrate 1 with which growth side bearing consists of silicon carbide of the hexagonal system which is the <0001> directions as seed crystal as well as an example 1 was prepared, and seed crystal was attached in the inner surface of the lid 4 of the crucible 3 made from a graphite. Next, although the interior of the crucible 3 made from a graphite was filled up with the raw material 2, the carbide (B4C) of the boron which is the impurity of P type was mixed 0.25% of the weight in the silicon carbide raw material in this case. (4) which generally mixes the compound containing (3) dopant element which uses for a raw material what sintered further the mixture of (2) and (1) which mix the (1) dopant element itself in a silicon carbide raw material as the method of mixing to the silicon carbide raw material of a dopant atom (equivalent to this example) -- the four approaches of ** using the silicon carbide raw material which doped the dopant element beforehand can be considered.
[0025] Evacuation after raw material restoration, temperature control, pressure control, etc. were performed almost like the example 1. However, the controlled atmosphere was made into Ar100%. It is necessary to set it as 0.1 - 1% of range as a charge of B4C in a silicon carbide raw material. The low concentration of supply of a dopant on a front face is more inadequate than this, the diffusion prevention effectiveness of the molecular species which contributes to growth cannot be expected, and good single crystal growth cannot be realized by high concentration from this.
[0026] In this way, when an X diffraction and Raman scattering analyzed the obtained silicon carbide monocrystal, it has checked that the silicon carbide monocrystal of hexagonal system had grown. The grown-up crystal was more uniform than the seed crystal top to the growth outermost surface, and there were also dramatically few abnormalities about carbon, and it was silicon carbide monocrystal of high quality. Furthermore, when the boron concentration under crystal was investigated according to secondary ion mass spectrometry, it was 3x1019cm-3.
[0027] Moreover, it considered as the {0001} side wafer by cutting and grinding the grown-up single crystal ingot in order to evaluate a micro pipe defect. Then, when the wafer front face was etched by the melting KOH of about 530 Centigrade and the microscope investigated the number of the forward large-sized hexagon etch pits corresponding to a micro pipe defect, compared with the case where only Ar is used as a controlled atmosphere, it turned out that the micro pipe defect is decreasing 30 to 40%. Moreover, it checked that the path of the generated micro pipe was decreasing by microscope observation of the front face before etching.

[Translation done.]

DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]
[Drawing 1] It is the block diagram showing an example of the single crystal growth equipment used for the manufacture approach of this invention.
[Description of Notations]
1 -- Silicon-carbide-monocrystal substrate (seed crystal),
2 -- Silicon carbide powder raw material,
3 -- Crucible made from a graphite,
4 -- Crucible lid made from a graphite,
5 -- Duplex quartz tube,
6 -- Bearing bar,
7 -- Felt made from a graphite,
8 -- Work-piece coil,
9 -- Ar gas piping,
10 -- Massflow controller for Ar gas,
11 -- Impurity gas piping,
12 -- Massflow controller for impurity gas,
13 -- Evacuation equipment.

[Translation done.]

* NOTICES *

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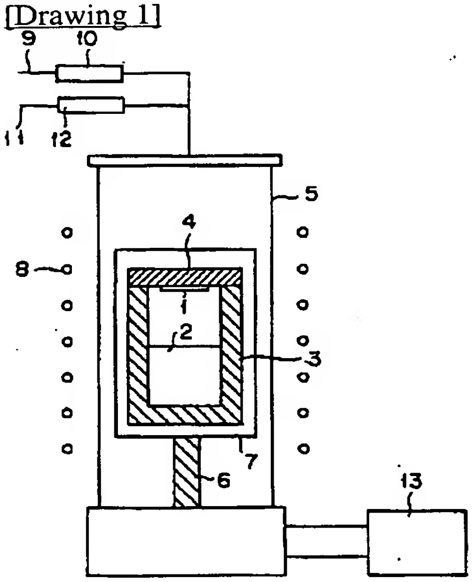
1.This document has been translated by computer. So the translation may not reflect the original precisely.
2.**** shows the word which can not be translated.
3.In the drawings, any words are not translated.

DRAWINGS

[Drawing 1]



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最終頁に続く

(54)【発明の名称】　単結晶炭化珪素の製造方法

(57)【要約】
【課題】　マイクロパイプ欠陥の少ない良質な単結晶炭化珪素を成長させる方法の提供。
【解決手段】　種結晶を用いた昇華再結晶法で炭化珪素単結晶を成長させる方法において、成長雰囲気中に不純物元素を含有させ、成長表面および成長結晶中に多量の不純物を供給することにより、マイクロパイプ欠陥の少ない炭化珪素単結晶を成長させる。

【特許請求の範囲】

【請求項１】　種結晶を用いた昇華再結晶法で炭化珪素単結晶を成長させる方法において、成長雰囲気中に不純物元素を含有させ、成長表面および成長結晶中に多量の不純物を供給し、マイクロパイプ欠陥の少ない炭化珪素単結晶を成長させる方法。

【請求項２】　前記成長雰囲気中の不純物として窒素、アルミニウム、あるいはホウ素原子を高濃度に含有させ、その結果、炭化珪素単結晶中に窒素、アルミニウム、あるいはホウ素原子を10^{19}cm^{-3}以上含有させせることにより、マイクロパイプ欠陥の少ない炭化珪素単結晶を成長することを特徴とする請求項１記載の単結晶炭化珪素の製造方法。

【発明の詳細な説明】

【０００１】

【発明の属する技術分野】本発明は、炭化珪素単結晶の製造方法に係わり、特に、青色発光ダイオードや電子デバイスなどの基板ウェハとなる良質で大型の単結晶インゴットの成長方法に関するものである。

【０００２】

【従来の技術】炭化珪素（ＳｉＣ）は耐熱性及び機械的強度も優れ、放射線に強いなどの物理的、化学的性質から耐環境性半導体材料として注目されている。特に６Ｈ型の炭化珪素結晶は室温で約３ｅＶの禁制帯幅を持ち、青色発光ダイオード材料として用いられている。

【０００３】しかしながら、大面積を有する高品質の炭化珪素単結晶を、工業的規模で安定に供給し得る結晶成長技術は、いまだ確立されていない。それゆえ、炭化珪素は、上述のような多くの利点及び可能性を有する半導体材料にもかかわらず、その実用化が阻まれていた。

【０００４】従来、研究室程度の規模では、例えば昇華再結晶法（レーリー法）で炭化珪素単結晶を成長させ、半導体素子の作製が可能なサイズの炭化珪素単結晶を得ていた。しかしながら、この方法では、得られた単結晶の面積が小さく、その寸法及び形状を高精度に制御することは困難である。また、炭化珪素が有する結晶多形及び不純物キャリア濃度の制御も容易ではない。

【０００５】また、化学気相成長法（ＣＶＤ法）を用いて珪素（Ｓｉ）等などの異種基板上にヘテロエピタキシャル成長させることにより立方晶の炭化珪素単結晶を成長させることも行われている。この方法では、大面積の単結晶は得られるが、基板との格子不整合が約２０％もあること等により多くの欠陥を含む（～10^{7}ｃｍ$^{-2}$）炭化珪素単結晶しか成長させることができず、高品質の炭化珪素単結晶を得ることは容易でない。

【０００６】これらの問題点を解決するために、種結晶を用いて昇華再結晶を行う改良型のレーリー法が提案されている（Yu.M. Tairov and V.F. Tsvetkov, Journal of Crystal Growth vol.52 (1981) pp.146-150）。この方法では、種結晶を用いているため結晶の核形成過程の制御が可能であり、また不活性ガスにより雰囲気圧力を数Ｔｏｒｒから１００Ｔｏｒｒ程度に制御することにより結晶の成長速度等を再現性良くコントロールできる。さらに、結晶の抵抗率、すなわち結晶中の不純物量は、不活性ガスからなる雰囲気中に不純物ガスを添加する、あるいは炭化珪素原料粉末中に不純物元素あるいはその化合物を混合することにより、制御可能である。この際、古賀　和幸、半導体研究第39巻 p.151に開示されているように、結晶の抵抗率は、結晶に窒素、アルミニウム、あるいはホウ素原子を10^{16}～10^{19}ｃｍ$^{-3}$導入することにより、０．０４～２００Ωｃｍの範囲で制御されていた。

【０００７】このように、種結晶を用いた昇華再結晶法を用いれば、結晶多形（ポリタイプ）、形状及び抵抗率を制御しながら、大型の炭化珪素単結晶を再現性良く成長させることができる。

【０００８】

【発明が解決しようとする課題】上記従来方法で炭化珪素単結晶を成長した場合、マイクロパイプ欠陥と呼ばれる結晶を成長方向に貫通する直径数ミクロンのピンホールが10^{2}～10^{3}ｃｍ$^{-2}$程度成長結晶に含まれていた。P.G. Neudeck et al., IEEE Electron Device Letters vol.15 (1994) pp.63-65に記載されているように、これらの欠陥は素子を作製した際に、漏れ電流等を引き起こし、その低減は炭化珪素単結晶のデバイス応用における最重要課題とされている。

【０００９】このマイクロパイプ欠陥は、J. Takahashi et al., Journal of Crystal Growth vol.135 (1994) pp.61-70に示されているように、炭化珪素単結晶において代表的な成長モードである渦巻成長に伴って発生している。

【００１０】本発明は上記事情に鑑みてなされたものであり、大型のウェハを切り出せる、欠陥が少なく良質の単結晶インゴットを再現性良く製造し得る炭化珪素単結晶の製造方法を提供するものである。

【００１１】

【課題を解決するための手段】上記目的を達成するための本発明は、次のように構成されている。

【００１２】請求項１に記載の発明は、種結晶を用いた昇華再結晶法で炭化珪素単結晶を成長させる方法において、成長雰囲気中に不純物元素を含有させ、成長表面および成長結晶中に多量の不純物を供給し、マイクロパイプ欠陥の少ない炭化珪素単結晶を成長させる方法である。

【００１３】請求項２に記載の発明は、前記成長雰囲気中の不純物として窒素、アルミニウム、あるいはホウ素原子を高濃度に含有させ、その結果、炭化珪素単結晶中に窒素、アルミニウム、あるいはホウ素原子を10^{19}cm^{-3}以上含有させせることにより、マイクロパイプ欠陥の少ない炭化珪素単結晶を成長することを特徴とする請求項１

記載の単結晶炭化珪素の製造方法である。

【００１４】本発明の単結晶炭化珪素の製造方法は、炭化珪素からなる原材料を加熱昇華させ、炭化珪素単結晶からなる種結晶上に供給し、この種結晶上に炭化珪素単結晶を成長する方法において、成長雰囲気中に不純物を高濃度に含有させることにより、成長表面に多量の不純物を供給し、結晶中の不純物濃度が$１０^{19}ｃｍ^{-3}$以上の炭化珪素単結晶を成長する。

【００１５】

【発明の実施の形態】本発明の製造方法では、成長雰囲気中に高濃度で不純物を含有させ、成長表面に多量の不純物を供給することによって炭化珪素単結晶の代表的な成長モードである渦巻成長を抑制し、マイクロパイプの発生を防止しようとするものである。渦巻成長は、成長に寄与する分子種が表面上を充分拡散した後、螺旋転位によって表面に形成されたステップに到達し、結晶格子に取り込まれることによって起こる。これは、通常ステップフローモードと呼ばれる結晶成長様式に相当する。発明者らは、表面に多量の不純物が存在する場合には、成長に寄与する分子種の表面拡散が阻害され、さらには不純物が効果的な二次元核形成の種となるために、このステップフローモードが起こり難く、マイクロパイプ発生が抑制されることを見出した。これは、成長に寄与する分子種がステップに到達せず、表面で二次元核形成を起こした場合には、螺旋転位によって表面に形成されたステップは渦を巻くことなく、そのままの形状で引き継がれ、結果として渦巻成長が抑制されるためである。

【００１６】また、改良レーリー法による炭化珪素成長中に、不純物を多量に表面に供給した結果、炭化珪素は高濃度の不純物（$１０^{19}ｃｍ^{-3}$以上）を含有することになり、その表面エネルギーは増加する。Frank (F.C. Frank, Acta Cryst. vol. 4 (1951) pp. 497-501) によれば、表面エネルギーの大きい物質ではマイクロパイプ径が小さくなる。従って、本発明によれば、マイクロパイプの発生を抑制できるだけでなく、発生したマイクロパイプの径を小さくし、デバイスへの影響を低減することも可能である。

【００１７】成長雰囲気中に不純物を高濃度に含有させる方法としては、ガスとして不活性ガスと共に反応槽に導入する方法と、炭化珪素粉末原料中に予め含有させておく方法の二つが考えられる。また従来、このような炭化珪素単結晶への不純物の導入は結晶の電気的特性（伝導型、抵抗率）を変化させる目的で、通常$１０^{16}ｃｍ^{-3}$から$10^{19}ｃｍ^{-3}$以下の範囲で行われていたが、本発明のように結晶欠陥の制御を目的として$１０^{19}ｃｍ^{-3}$以上の範囲で用いられたことはない。

【００１８】

【実施例１】図１は、種結晶を用いた改良型レーリー法によって単結晶炭化珪素を成長させる本発明に用いられる製造装置の一例である。

【００１９】まず、この単結晶成長装置について簡単に説明する。結晶成長は、種結晶として用いた炭化珪素単結晶基板１の上に、原料である炭化珪素粉末２を昇華再結晶させることにより行われる。種結晶の炭化珪素結晶基板１は、黒鉛製坩堝３の蓋４の内面に取り付けられる。原料の炭化珪素粉末２は、黒鉛製坩堝３の内部に充填されている。このような黒鉛製坩堝３は、二重石英管５の内部に、黒鉛の支持棒６により設置される。黒鉛製坩堝３の周囲には、熱シールドのための黒鉛製フェルト７が設置されている。二重石英管５は、真空排気装置により高真空排気（１０^{-5}Ｔｏｒｒ以下）でき、かつ内部雰囲気をＡｒとドーパントガスの混合ガスにより圧力制御することができる。また、二重石英管５の外周には、ワークコイル８が設置されており、高周波電流を流すことにより黒鉛製坩堝３を加熱し、原料及び種結晶を所望の温度に加熱することができる。坩堝温度の計測は、坩堝上部及び下部を覆うフェルトの中央部に直径２～４ｍｍの光路を設け坩堝上部及び下部からの光を取りだし、二色温度計を用いて行う。坩堝下部の温度を原料温度、坩堝上部の温度を種温度とする。

【００２０】次に、この結晶成長装置を用いた炭化珪素単結晶の製造について実施例を説明する。

【００２１】まず、種結晶として、成長面方位が＜０００１＞方向である六方晶系の炭化珪素からなる基板１を用意した。そして、この基板１を黒鉛製坩堝３の蓋４の内面に取り付けた。また、黒鉛製坩堝３の内部には、原料２を充填した。次いで、原料を充填した黒鉛製坩堝３を、種結晶を取り付けた蓋４で閉じ、黒鉛製フェルト７で被覆した後、黒鉛製支持棒６の上に乗せ、二重石英管５の内部に設置した。そして、石英管の内部を真空排気した後、ワークコイルに電流を流し原料温度を摂氏２０００度まで上げた。その後、雰囲気ガスとしてＡｒガスに窒素ガスを７５％含んだ混合ガスを流入させ、石英管内圧力を約６００Ｔｏｒｒに保ちながら、原料温度を目標温度である摂氏２４００度まで上昇させた。成長圧力である２０Ｔｏｒｒには約３０分かけて減圧し、その後約２０時間成長を続けた。この際の成長速度は約１ｍｍ毎時であった。成長中の窒素ガスの割合はＡｒガス等の不活性ガスに対し、１０～１００％の範囲に設定する必要がある。これより低濃度では、表面へのドーパントの供給が不十分であり成長に寄与する分子種の拡散防止効果が期待できず、単結晶中の窒素濃度も$１０^{19}ｃｍ^{-3}$以上にはならない。また、窒素の反応槽内の分圧が４０Ｔｏｒｒ以上になると、成長表面上の窒素が結晶性に悪影響を及ぼすようになる。すなわち、多結晶化等が起こるようになる。

【００２２】こうして得られた炭化珪素単結晶をＸ線回折及びラマン散乱により分析したところ、六方晶系の炭化珪素単結晶が成長したことを確認できた。成長した結晶は種結晶上より成長最表面まで均一で、また炭素に関

する異常物も非常に少なく、高品質の炭化珪素単結晶であった。さらに、二次イオン質量分析法により結晶中の窒素濃度を調べたところ、２×１０^{20}ｃｍ$^{-3}$であった。

【００２３】また、マイクロパイプ欠陥を評価する目的で、成長した単結晶インゴットを切断、研磨することにより｛０００１｝面ウェハとした。その後、摂氏約５３０度の溶融ＫＯＨでウェハ表面をエッチングし、顕微鏡によりマイクロパイプ欠陥に対応する大型の正六角形エッチピットの数を調べたところ、Ａｒのみを雰囲気ガスとして用いた場合に比べ、マイクロパイプ欠陥が半減していることがわかった。また、発生したマイクロパイプの径が減少しているのがエッチング前表面の顕微鏡観察により確認できた。

【００２４】

【実施例２】実施例１と同じく、種結晶として、成長面方位が<０００１>方向である六方晶系の炭化珪素からなる基板１を用意し、種結晶を黒鉛製坩堝３の蓋４の内面に取り付けた。次に、黒鉛製坩堝３の内部に、原料２を充填したが、この際、炭化珪素原料中にＰ型の不純物である硼素の炭化物（B_4C）を０．２５重量%混合させた。一般的に、ドーパント原子の炭化珪素原料への混合の仕方としては、（１）ドーパント元素そのものを炭化珪素原料に混合する、（２）（１）の混合物をさらに焼結したものを原料に用いる、（３）ドーパント元素を含む化合物を混合する（この実施例に相当）、（４）予めドーパント元素をドープした炭化珪素原料を用いる、の４つの方法が考えられる。

【００２５】原料充填以後の真空排気、温度制御、圧力制御等は実施例１とほぼ同様に行った。ただし、雰囲気ガスはＡｒ１００％とした。炭化珪素原料中のB_4Cの仕込み量としては、０．１～１％の範囲に設定する必要がある。これより低濃度では、表面へのドーパントの供給が不十分であり成長に寄与する分子種の拡散防止効果が期待できず、またこれより高濃度では良質な単結晶成長が実現できない。

【００２６】こうして得られた炭化珪素単結晶をＸ線回折及びラマン散乱により分析したところ、六方晶系の炭化珪素単結晶が成長したことを確認できた。成長した結晶は種結晶上より成長最表面まで均一で、また炭素に関する異常物も非常に少なく、高品質の炭化珪素単結晶であった。さらに、二次イオン質量分析法により結晶中のホウ素濃度を調べたところ、３×１０^{19}ｃｍ$^{-3}$であった。

【００２７】また、マイクロパイプ欠陥を評価する目的で、成長した単結晶インゴットを切断、研磨することにより｛０００１｝面ウェハとした。その後、摂氏約５３０度の溶融ＫＯＨでウェハ表面をエッチングし、顕微鏡によりマイクロパイプ欠陥に対応する大型の正六角形エッチピットの数を調べたところ、Ａｒのみを雰囲気ガスとして用いた場合に比べ、マイクロパイプ欠陥が３０～４０％減少していることがわかった。また、発生したマイクロパイプの径が減少しているのをエッチング前表面の顕微鏡観察により確認した。

【００２８】

【発明の効果】以上説明したように、請求項１および請求項２に記載の発明によれば、種結晶を用いた改良型レーリー法において、渦巻成長を抑制し、これらが原因となって発生するマイクロパイプが少ない良質の炭化珪素単結晶を再現性、及び均質性良く成長させることができる。

【００２９】このような炭化珪素単結晶を成長用基板として用い、気相エピタキシャル成長法により、この基板上に炭化珪素単結晶薄膜を成長させれば、光学的特性の優れた青色発光素子、電気的特性の優れた高耐圧・耐環境性電子デバイスを製作することができる。

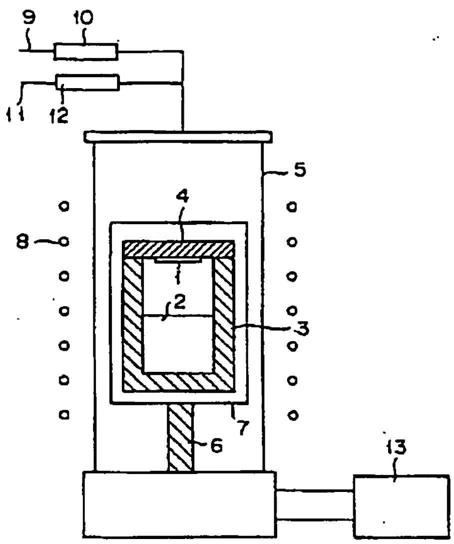
【図面の簡単な説明】

【図１】　本発明の製造方法に用いられる単結晶成長装置の一例を示す構成図である。

【符号の説明】

１…炭化珪素単結晶基板（種結晶）、
２…炭化珪素粉末原料、
３…黒鉛製坩堝、
４…黒鉛製坩堝蓋、
５…二重石英管、
６…支持棒、
７…黒鉛製フェルト、
８…ワークコイル、
９…Arガス配管、
１０…Arガス用マスフローコントローラ、
１１…不純物ガス配管、
１２…不純物ガス用マスフローコントローラ、
１３…真空排気装置。

【図１】



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